CLAIMS

- 1. An in-spray glow discharge ionization method comprising the steps of:
- (a) supplying a gas exhibiting Penning effect so as to surround a fluid containing a compound to be measured for forming an nebulized flow of the fluid; and
- (b) generating glow discharge in the nebulized flow to generate cations of the gas exhibiting Penning effect and excited atoms exhibiting Penning effect so as to ionize a chemical substance having low ionization probability with high sensitivity, directly or indirectly through an intermediately generated chemical species.
- 2. The in-spray glow discharge ionization method according to Claim 1, wherein the nebulized flow is heated.
- 3. The in-spray glow discharge ionization method according to Claim 1, wherein a rare gas is used as the gas exhibiting Penning effect.
- 4. The in-spray glow discharge ionization method according to Claim 3, wherein argon is used as the rare gas.
 - 5. The in-spray glow discharge ionization method

according to Claim 4, wherein the rare gas is argon (Ar), and argon cations $({\rm Ar}^{\dagger})$ and excited argon $({\rm Ar}^{\star})$ are generated.

- 6. The in-spray glow discharge ionization method according to Claim 1, further comprising blowing a dry gas in order to dry the nebulized flow.
- 7. The in-spray glow discharge ionization method according to Claim 6, wherein a nitrogen gas, air, or a rare gas is used as the dry gas.
- 8. An in-spray glow discharge ionization apparatus comprising:
- (a) a supply port supplying a fluid containing a compound to be measured;
- (b) a gas blowing port which surrounds the supply port and which blows a gas exhibiting Penning effect to nebulize the fluid supplied from the supply port;
- (c) a ground-side discharge electrode provided at a generation port at which the nebulized flow is generated; and
- (d) a voltage application-side discharge electrode which is disposed in the traveling direction of the nebulized flow and opposed to the ground-side discharge

electrode;

wherein measurement is performed using a mass spectrometer by ionizing components of the compound to be measured which constitutes the fluid using a cationized and excited gas exhibiting Penning effect while the fluid is being nebulized by the gas exhibiting Penning effect.

- 9. The in-spray glow discharge ionization apparatus according to Claim 8, further comprising a dry gas blowing port for drying the nebulized flow provided around or in the vicinity of the supply port and the gas blowing port for blowing a gas exhibiting Penning effect for nebulizing the fluid.
- 10. The in-spray glow discharge ionization apparatus according to Claim 8, wherein the gas exhibiting Penning effect is a rare gas.
- 11. The in-spray glow discharge ionization apparatus according to Claim 10, wherein the rare gas is He, Ne, Ar, Kr or Xe.
- 12. The in-spray glow discharge ionization apparatus according to Claim 8, wherein the compound to be measured is a chemical substance which has low ionization probability.

- 13. The in-spray glow discharge ionization apparatus according to Claim 12, wherein the chemical substance is an aromatic nitro compound, oxine copper, halogenated nitrobenzyl, or a polycyclic aromatic hydrocarbon.
- 14. The in-spray glow discharge ionization apparatus according to Claim 9, wherein the dry gas is nitrogen, air, or a rare gas.
- 15. The in-spray glow discharge ionization apparatus according to Claim 8, wherein a surface of at least one of the discharge electrodes is covered with a substance which has low oxidation state.
- 16. The in-spray glow discharge ionization apparatus according to Claim 15, wherein the substance which has low oxidation state is gold, platinum, or silver.
- 17. The in-spray glow discharge ionization apparatus according to Claim 8, wherein the voltage application-side discharge electrode includes a plurality of electrodes.
- 18. The in-spray glow discharge ionization apparatus according to Claim 17, wherein each of said plurality of

electrodes is a needle-shaped electrode.

- 19. The in-spray glow discharge ionization apparatus according to Claim 17 or 18, wherein a tertiary actuator is provided for adjusting three-dimensional positions of the electrodes.
- 20. The in-spray glow discharge ionization apparatus according to Claim 8, wherein electrical insulation is performed in an ion source except for the front end of the electrodes.